Exceptional service in the national interest

Sandia National Laboratories

Cheap, Abundant & Safe Materials =

Advanced Zinc-Manganese Oxide Alkaline Batteries

October 2017, San Diego, California

Timothy N. Lambert

Sandia National Laboratories

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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Grid Energy Storage

Need:
Safe, reliable, **low-cost** electrochemical storage

Intermittent sources requires storage

Alkaline Zn/MnO_2 Batteries

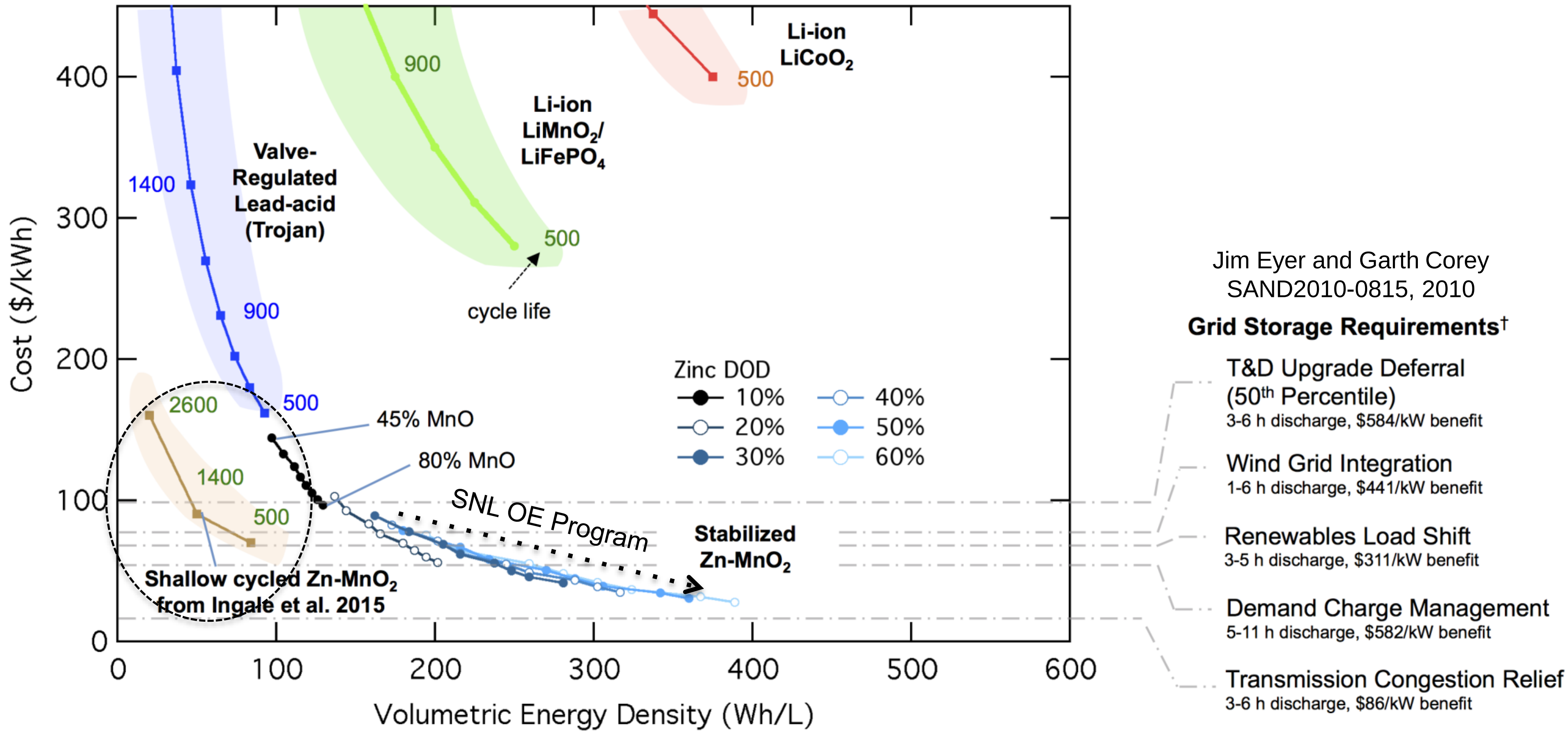
- **Cost**
  - Traditional primary batteries - $18 per kWh
  - Low-cost materials and manufacturing
  - Established supply chain
- **Safety**
  - Aqueous chemistry
  - Non-flammable
  - EPA certified for landfill disposal
- **Reliability**
  - Long shelf-life
  - Limited thermal management required

www.solarindustrymag.com

Reversibility and Cycle life are the Challenges

Zn-MnO_2 Batteries for Grid Storage

Opportunity exists to Increase Capacity and Decrease Costs

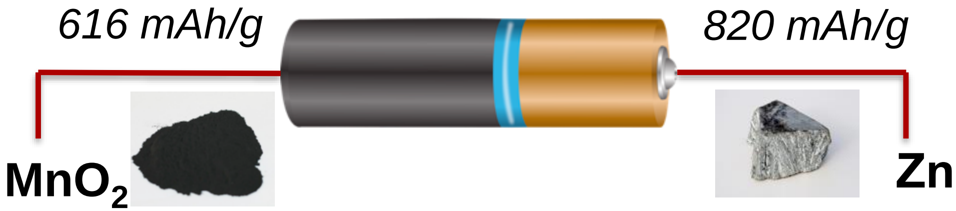


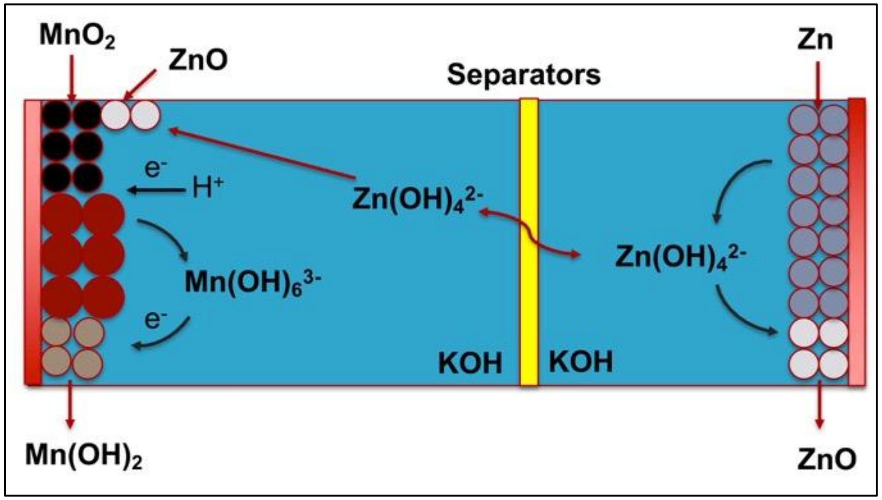
Toward Low Cost/High Volumetric Energy Storage

1. Support Limited Depth-of-Discharge Efforts
2. Develop Higher Capacity Batteries

N. D. Ingale, J. W. Gallaway, M. Nyce, A. Couzis and S. Banerjee, J. Power Sources, 276, 7 (2015).

Alkaline Zn/MnO_2 Batteries





<u>*Issues to be addressed*</u>

Cathode:
- Irreversibility of Cathode
- Susceptibility to Zinc poisoning

Separator:
- Zincate crossover

Anode:
- Shape Change
- Dendrite Growth
- Irreversible ZnO Passivation

Limiting Depth of Discharge has been shown to be a viable approach

N. D. Ingale, J. W. Gallaway, M. Nyce, A. Couzis and S. Banerjee, J. Power Sources, 276, 7 (2015).

Full $2e^-$ can be stabilized but is still susceptible to zinc poisoning

G. G. Yadav, J. W. Gallaway, D. E. Turney, M. Nyce, J. Huang, X. Wei and S. Banerjee, Nat. Commun., 8, 14424 (2017).

The Team

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Michael Nyce
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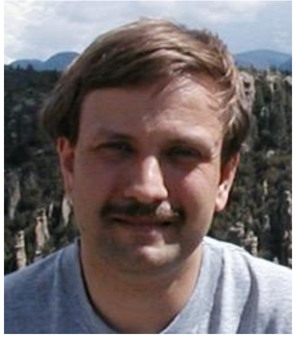

Professor Igor Vasiliev

Birendra A. Magar (LDRD funded)

Also leveraging SNL-LDRD and CINT Proposal

Summary for Project

FY 17 Accomplishments

1. Comprehensive study of electrolyte additive on limited DOD Zn/MnO_2 batteries: Extend battery lifetime by ~ 300 %
2. Developed new assay to determine zincate diffusion constants for separators
3. Examined use of zincate impermeable ceramic separator for limited DOD Zn/MnO_2 Batteries
4. Analysis of zinc cycle life: Increased DOD on zinc anode: > 500 cycles@15% DOD
5. Examined effect of charging protocols on Zn/MnO_2 cycle life
6. Development of a model describing the behavior of γ-MnO_2 in shallow-cycled Zn/MnO_2 batteries
7. Development of improved zincate blocking separators

Manuscripts

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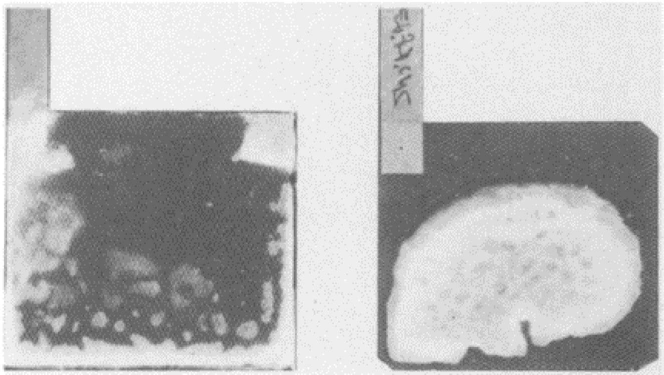
3. T. N. Lambert, J. A. Vigil, J. Duay and M. Kelly "Manganese oxide nanomaterials for electrocatalysis and energy storage" 253rd ACS National Meeting, San Francisco, CA, April 2-6th, 2017.

Other

1. "Understanding the electrochemical processes in alkaline Zn-MnO_2 batteries" CINT User Proposal accepted.

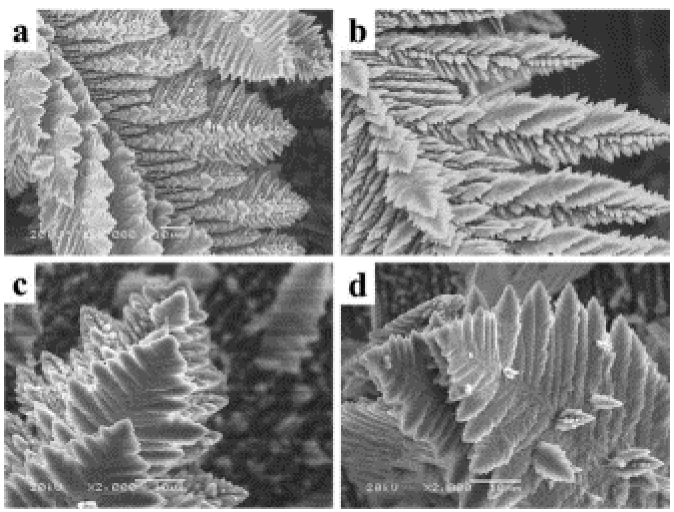
Anode

Shape Change



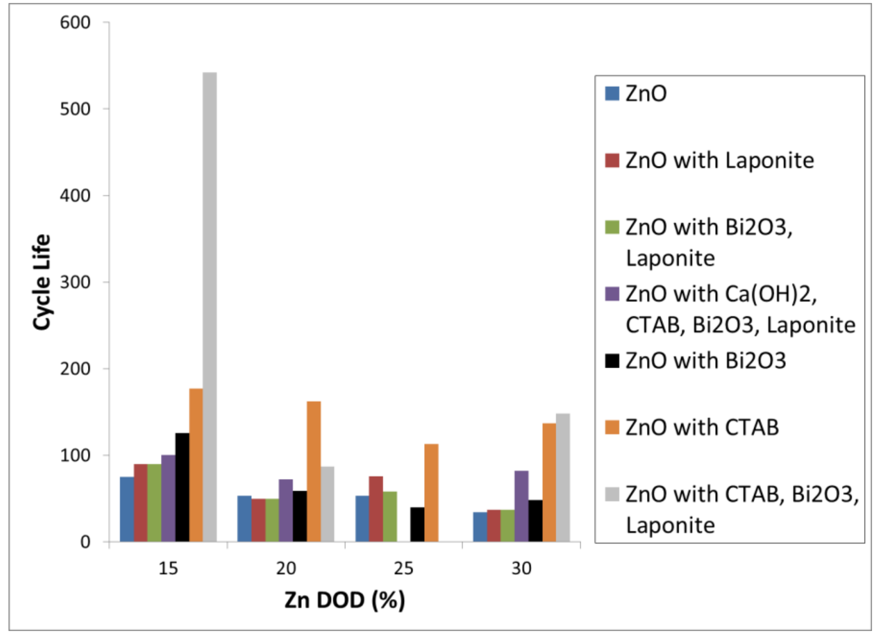
Journal of The Electrochemical Society, 138 (2) 645-664 (1991)

Dendrite Growth

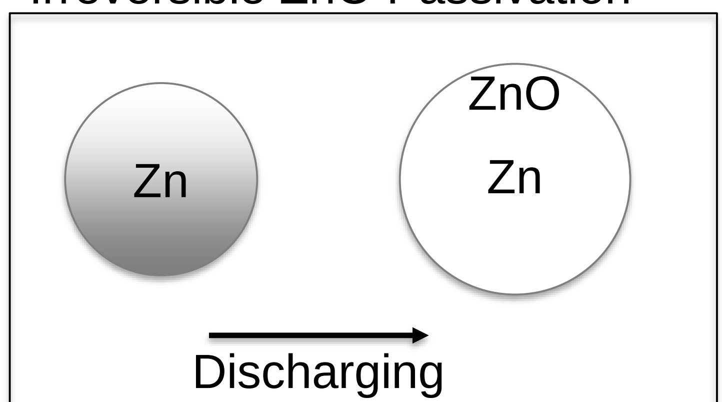


Journal of The Electrochemical Society, 163 (9) A1836-A1840 (2016)

Improved Anode DOD @ CUNY-EI



Irreversible ZnO Passivation



M. D'Ambrose *et al.* “Cycle Life Study and Failure Analysis of the Rechargeable Porous Zinc Electrode in Alkaline Electrolyte” *manuscript in preparation*.

Cathode

Theoretical Study of H Trapping by γ-MnO_2

Research Objectives

- Develop a model describing the behavior of γ-MnO_2 in shallow-cycled Zn/MnO_2 batteries.
- Examine structural changes occurring in γ-MnO_2 during the initial discharge reaction.
- Investigate the mechanism of formation of the α-MnOOH phase.
- Study the influence of DOD and the cycle life of rechargeable Zn/MnO_2 batteries.

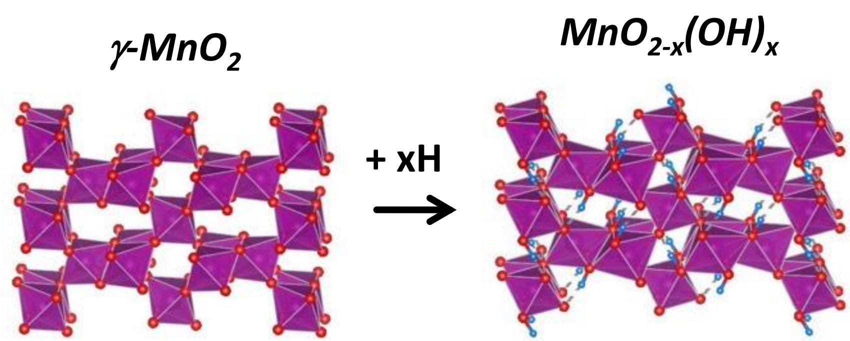
Computational Methods

- Quantum ESPRESSO* plane wave electronic structure code
- Density functional theory + ultra-soft pseudopotentials
- Revised generalized gradient approximation (PBEsol)

* http://www.quantum-espresso.org

Discharge reaction in the γ-MnO_2 cathode:

$$MnO_2 + xH_2O + xe^- \rightarrow MnO_{2-x}(OH)_x + xOH^-$$



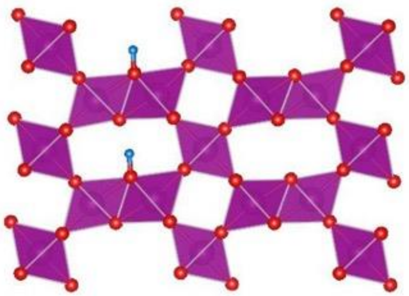
I. Vasiliev *et al.* "*Ab initio* studies of proton insertion in shallow-cycled gamma-MnO_2" *manuscript in preparation.*

DFT Modeling

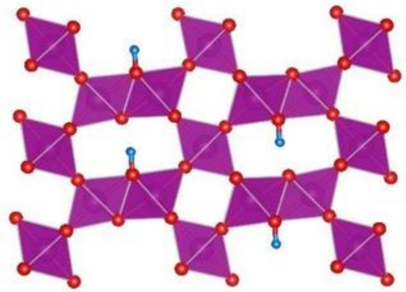
Theoretical Study of H Trapping by γ-MnO_2

Calculated Lowest Energy Structures of $MnO_{2-x}(OH)_x$ for $0 \le x \le 1$

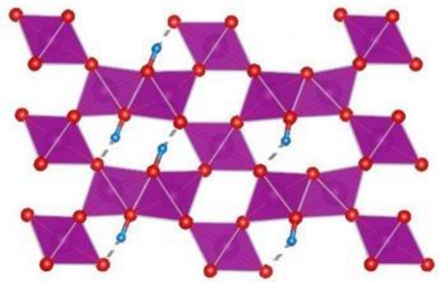
x = 1/6



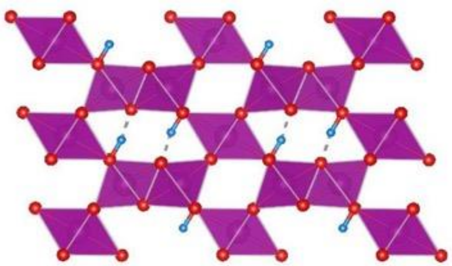
x = 1/3



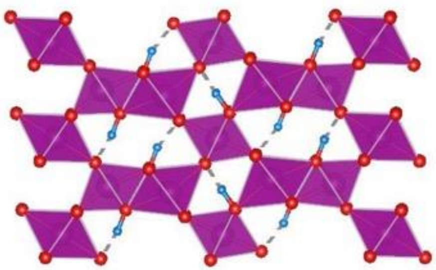
x = 1/2



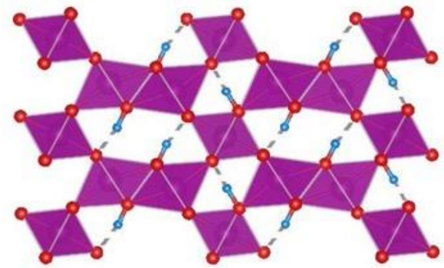
x = 2/3



x = 5/6



x = 1

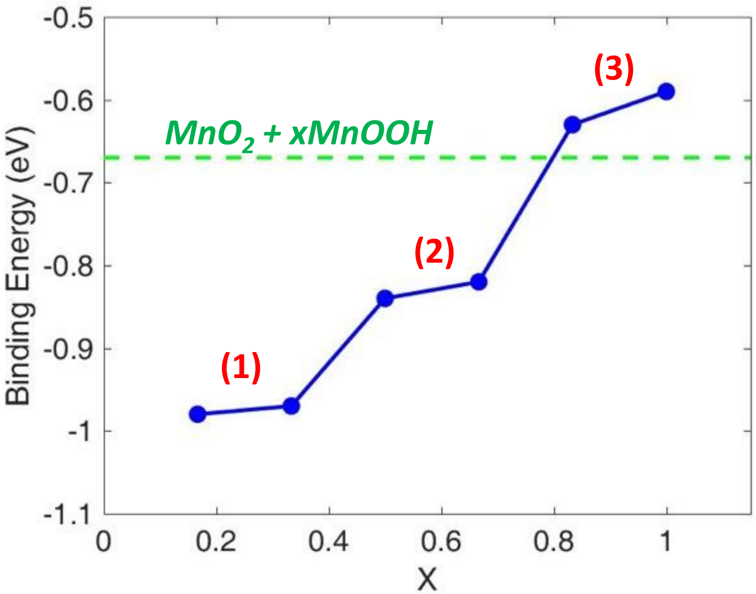


- Protonation produces significant structural distortions in γ-MnO_2.
- Energy of H-insertion is lower for 2x1 R-MnO_2 tunnels than for 1x1 β-MnO_2 tunnels.
- Protonation is carried out in three stages: (1) 1 H atom is inserted in each 2x1 tunnel, (2) 2 H atoms are inserted in each 2x1 tunnel, (3) 1 H atom is inserted in each 1x1 tunnel.

I. Vasiliev *et al.* "*Ab initio* studies of proton insertion in shallow-cycled gamma-MnO_2" *manuscript in preparation.*

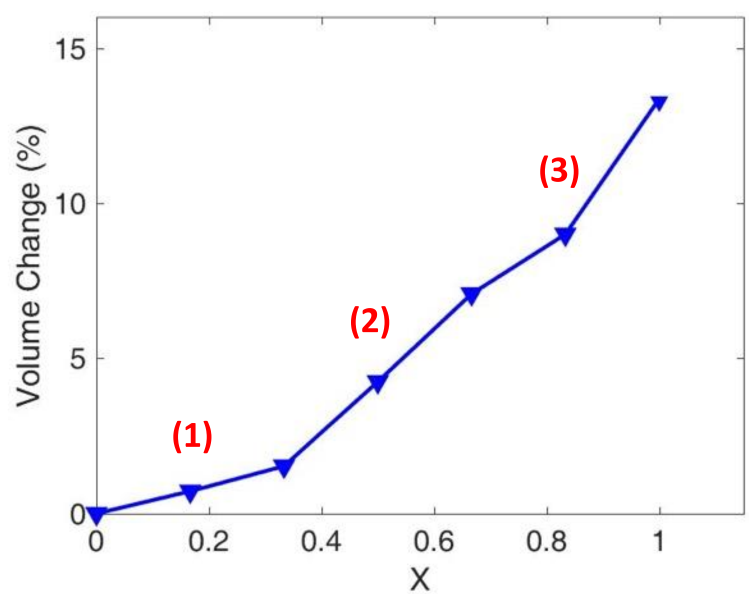
Theoretical Study of H Trapping by γ-MnO_2

Binding Energy per H Atom



$|E_b^{stage1}| > |E_b^{stage2}| > |E_b^{stage3}|$

Volume Expansion



$\Delta V^{stage1} < \Delta V^{stage2} < \Delta V^{stage3}$

- Binding energy per H atom decreases significantly with increasing DOD.
- Volume of protonated γ-MnO_2 phase increases nonlinearly with increasing DOD.
- Initially, inserted protons occupy 2x1 tunnels of γ-MnO_2 producing α-MnOOH.
- Protonation of 1x1 tunnels leads to structural breakdown of $MnO_{2-x}(OH)_x$.
- Battery life cycle can be extended by limiting protonation to 1 H atom per 2x1 tunnel.

TEA additive in limited DOD Zn/MnO_2

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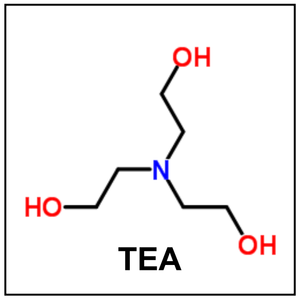
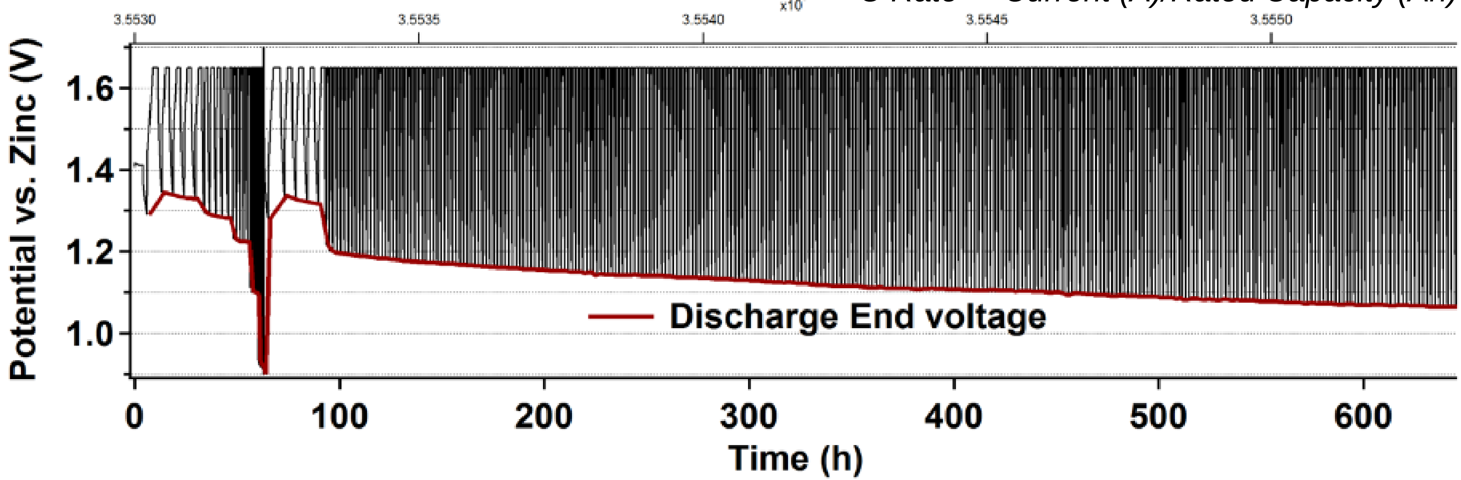
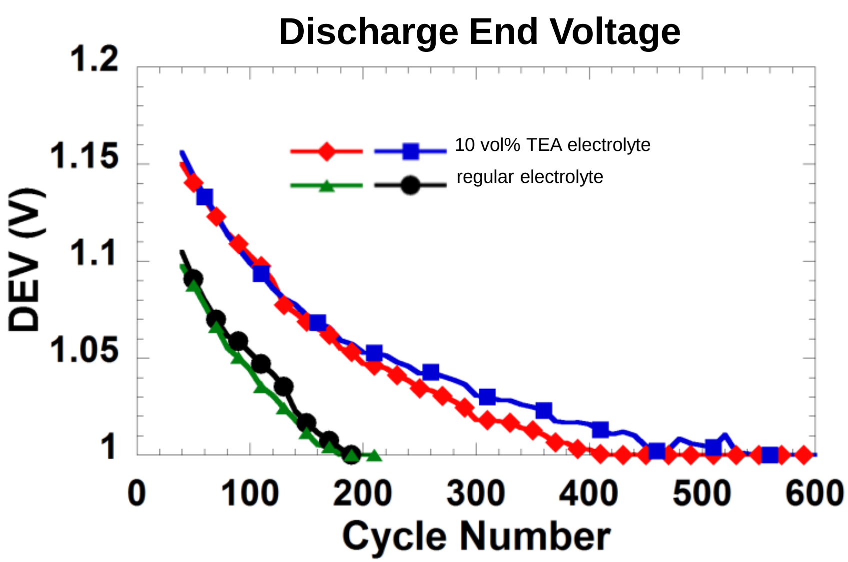
- Triethanolamine reported to complex w/ Mn^{3+} and Mn^{2+} in alkaline
- Previously examined for full 1e- and 2e- discharges
- Thought to impact only second e-

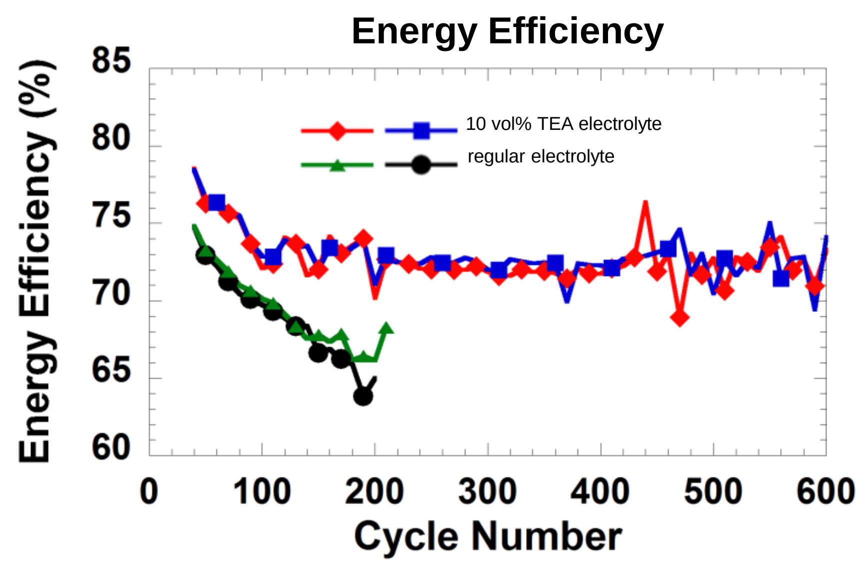
~ 130 mAh (MnO_2) cell, 10%DOD, C/5 discharge rate

C Rate = Current (A)/Rated Capacity (Ah)









J. Duay *et al.* “Effect of triethanolamine on rechargeable Zn/MnO_2 alkaline batteries under reduced depth of discharge conditions” *manuscript submitted.*

Need for Selective Separators

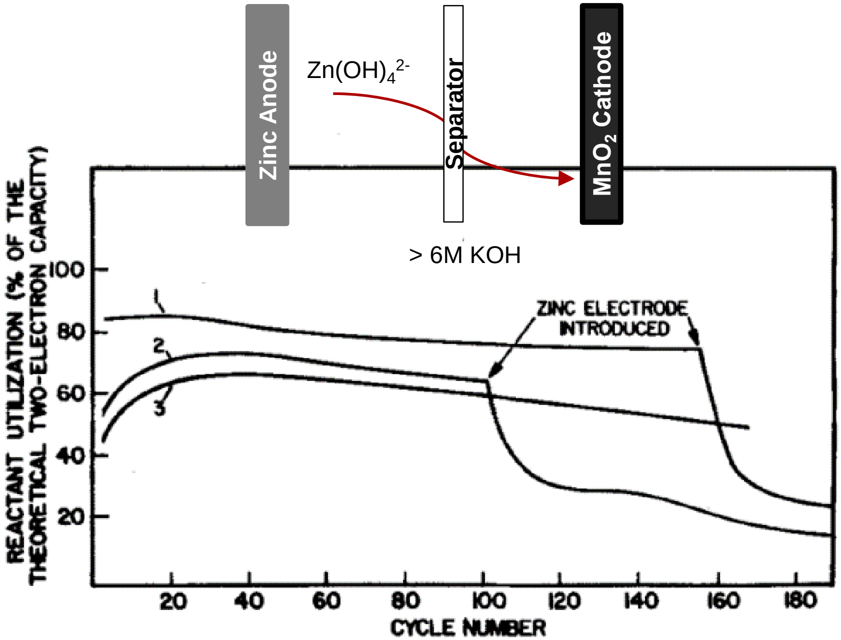
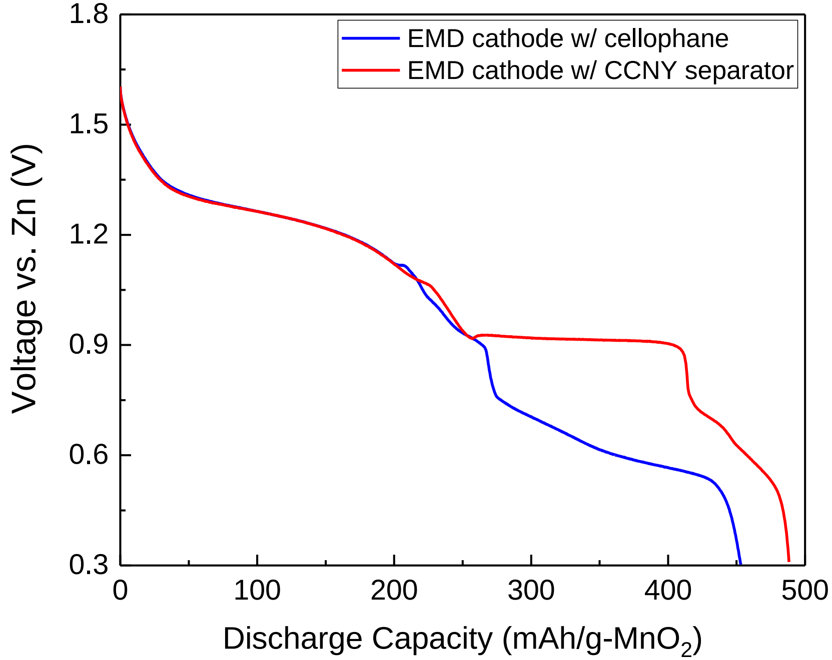


Fig. 5. Effect of the introduction of zinc on capacity retention of modified MnO_2 electrodes: 1) chemically modified electrode; 2) physically modified electrode; 3) physically modified electrode in 9M KOH + 0.1M $Zn(OH)_4^{=}$.

Voltage curves of Zn/EMD batteries achieving 2e$^-$ capacity (discharge end voltage = 0.3 V vs. Zn)



- Research by Ford in the 1980s showed that the MnO_2 cathode could be stabilized at low loadings ***in the absence of Zinc***
- New stabilized 2e- cathodes are 100% reversible ***in the absence of Zinc***

- Test of separator in “actual” conditions
- Complete battery build
- Requires slow discharge
- Only shows effect at 2nd e$^-$?

Imperative need for zincate blocking separators

Separators – Ceramic Separator

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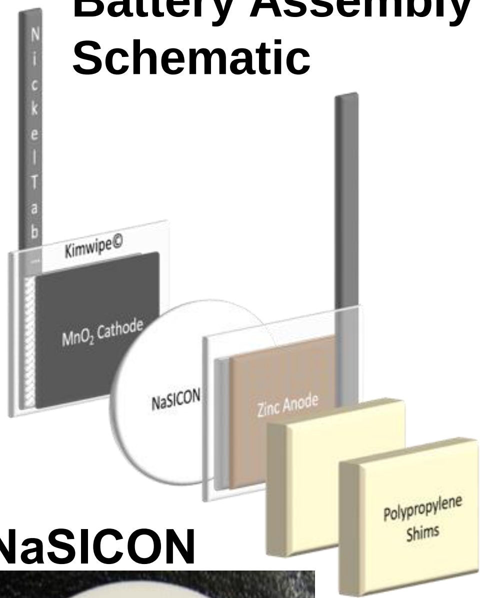
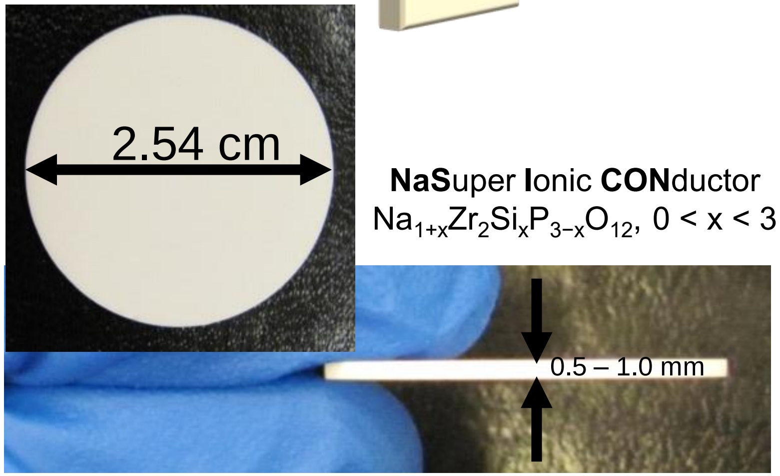
Battery Assembly Schematic



NaSICON



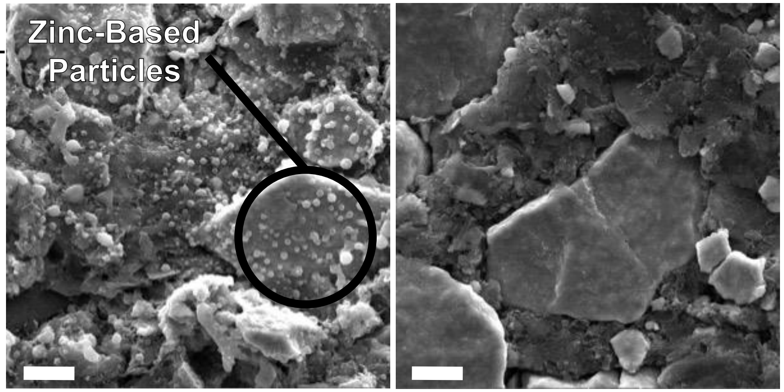
NaSuper **I**onic **CON**ductor
$Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$, $0 < x < 3$

NaSICON purchased from Ceramatec

SEM/EDS analysis after cycling

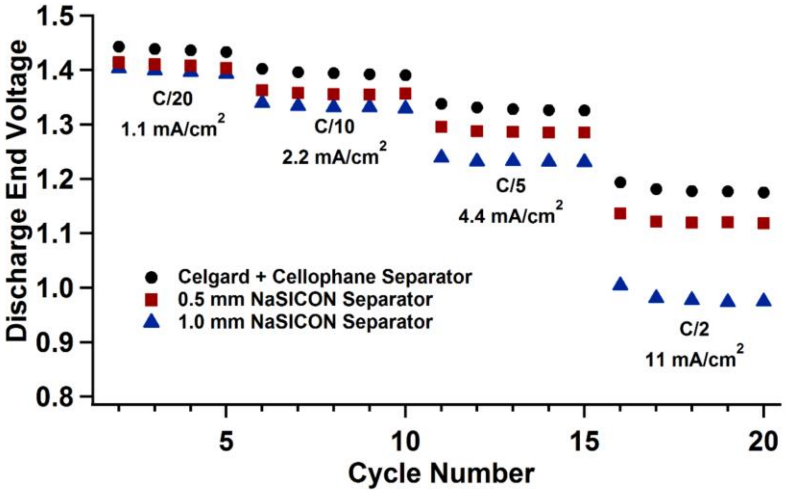
Celgard + Cellophane Separators | **1.0 mm NaSICON Separator**

Element	Atomic %
Au K	0.2
C K	43.9
F K	10.7
Mn K	9.8
Na K	1.5
O K	32.3
Zn K	**1.6**



Element	Atomic %
Au K	0.1
C K	43.6
F K	11.3
Mn K	10.8
Na K	0.9
O K	33.3
Zn K	**0.0**

Ceramic Separators in NaOH electrolyte are viable at low rates



J. Duay *et al. manuscript in preparation.*

Separators – New Analysis Method

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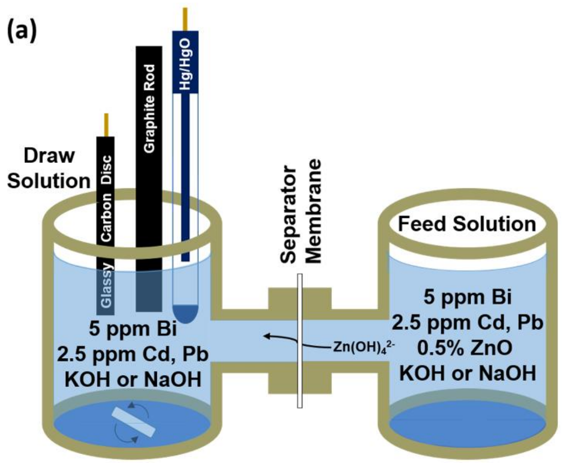
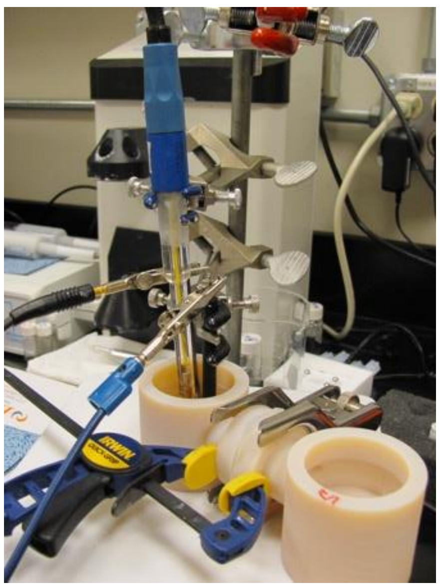
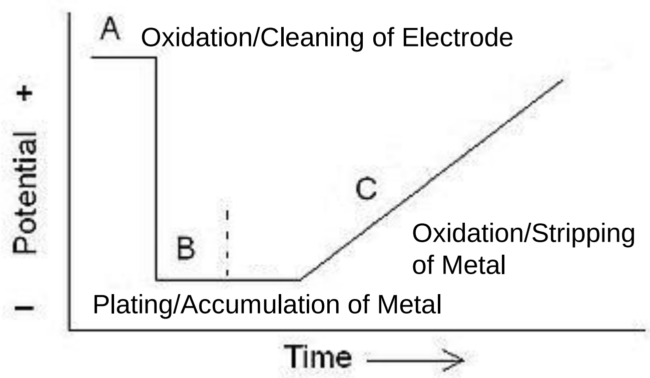
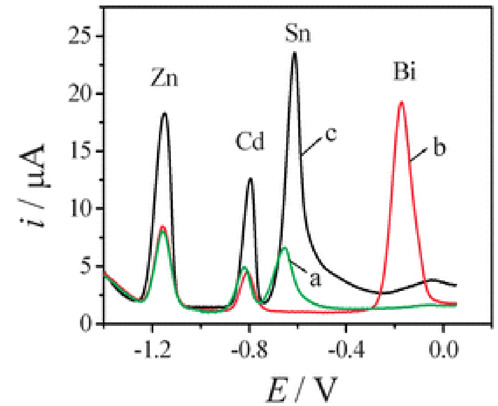




Special thanks to Eric Allcorn for help in designing and printing

Method utilizes Anodic Stripping Voltammetry

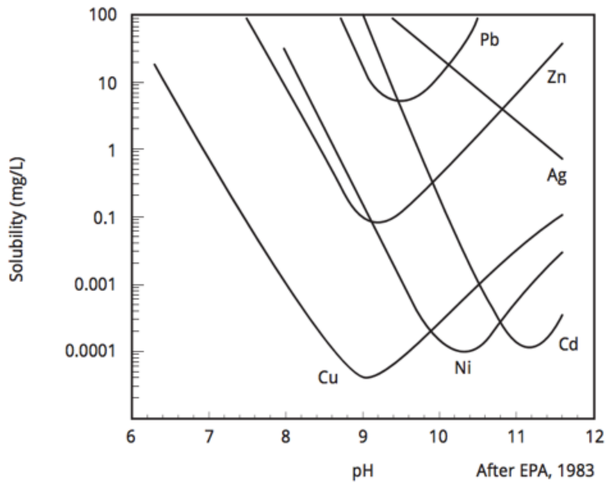




Analyst, 2012,**137**, 614-617

Sensitive - limits of detection (LOD): ppb levels
Selective - -different metals are resolved by their stripping/oxidation potential

Method utilizes hydroxide complexation/solubility



$$ZnO(s) + H_2O + 2OH^- \rightarrow Zn(OH)_4^{2-}$$

$$PbO(s) + H_2O + OH^- \rightarrow Pb(OH)_3^-$$

$$CdO(s) + H_2O + OH^- \rightarrow Cd(OH)_3^-$$

$$Bi_2O_3(s) + 3H_2O + 2OH^- \rightarrow 2Bi(OH)_4^-$$

First ever ASV method for zinc in alkaline

http://www.porexfiltration.com/learning-center/technology/precipitation-microfiltration/

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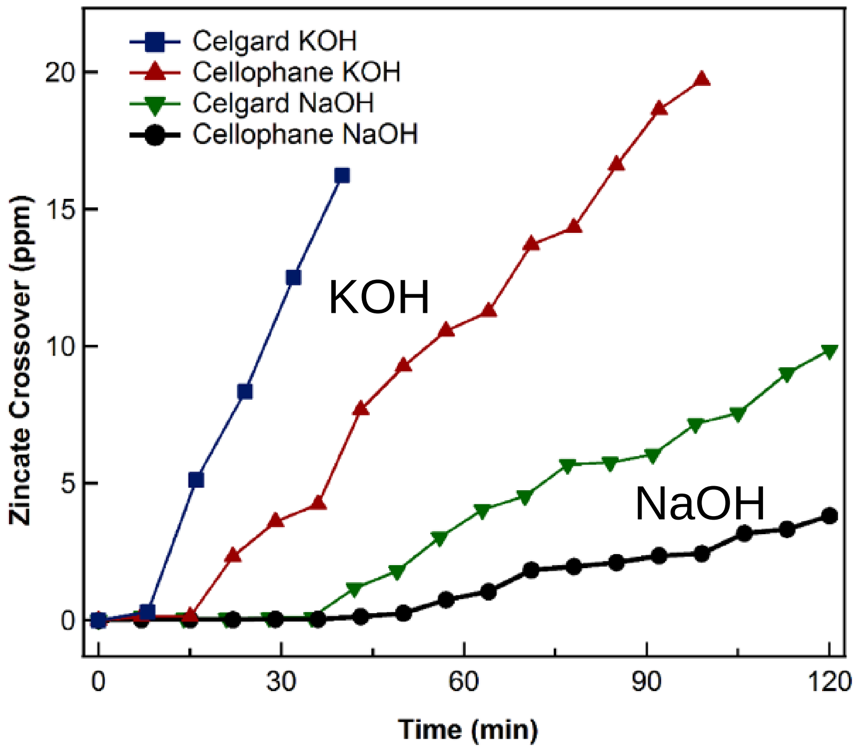
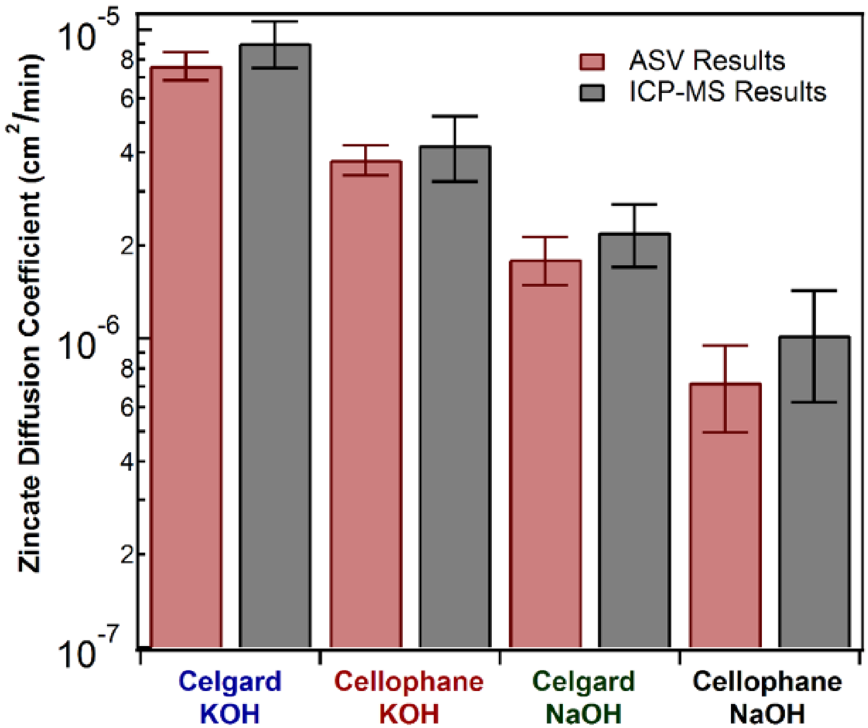
Separators





- Compares favorably *vs.* ICP and Complexometric methods
- Faster experiment times, very reproducible, low limit of detection
- First demonstration of ASV measurement of Zinc in alkaline
- Will allow for rapid screening of newly developed membranes

J. Duay *et al. "Stripping Voltammetry for the Real Time Determination of Zinc Membrane Diffusion Coefficients in High pH: Towards Rapid Screening of Alkaline Battery Separators" Electroanalysis 2017, http://dx.doi.org/10.1002/elan.201700337.*

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4. Analysis of zinc cycle life: Increased DOD on zinc anode: > 500 cycles@15% DOD
5. Examined effect of charging protocols on Zn/MnO_2 cycle life
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Other

1. "Understanding the electrochemical processes in alkaline Zn-MnO_2 batteries" CINT User Proposal accepted.

Advanced Zn-MnO_2 Alkaline Batteries

FY 18 Path Forward

1. Establish method for *in situ* Raman spectroscopic interrogation of Zn/MnO_2 cells
2. Develop optimized Zn anode with increased depth-of-discharge and cycle lifetime
3. Advanced separator development
4. Examine 2e- discharge of MnO_2 using zincate blocking membrane
5. Finish *ab initio* (DFT) model of hydrogen trapping by gamma-MnO_2 in shallow-cycled MnO_2 electrodes

Acknowledgements

Dr. Imre Gyuk, Energy Storage Program Manager, Office of Electricity Delivery and Energy Reliability is thanked for his financial support of this project.

Team Members

SNL	*CUNY-EI*	*NMSU*
Dr. Jonathon Duay	Prof. Sanjoy Banerjee	Prof. Igor Vasiliev
Maria Kelly	Dr. Damon Turney	Birendra Magar
Ruby Aidun	Dr. Gautum Yadav	
Julian Vigil	Michael D'Ambrose	
Dr. Eric Allcorn	Snehal Kohlekar	
(CINT)	Michael Nyce	
Dr. Brian Swartzentruber	Jinchao Huang	
Dr. Katherine Jungjohann		

Zn-MnO_2 Batteries for Grid Storage

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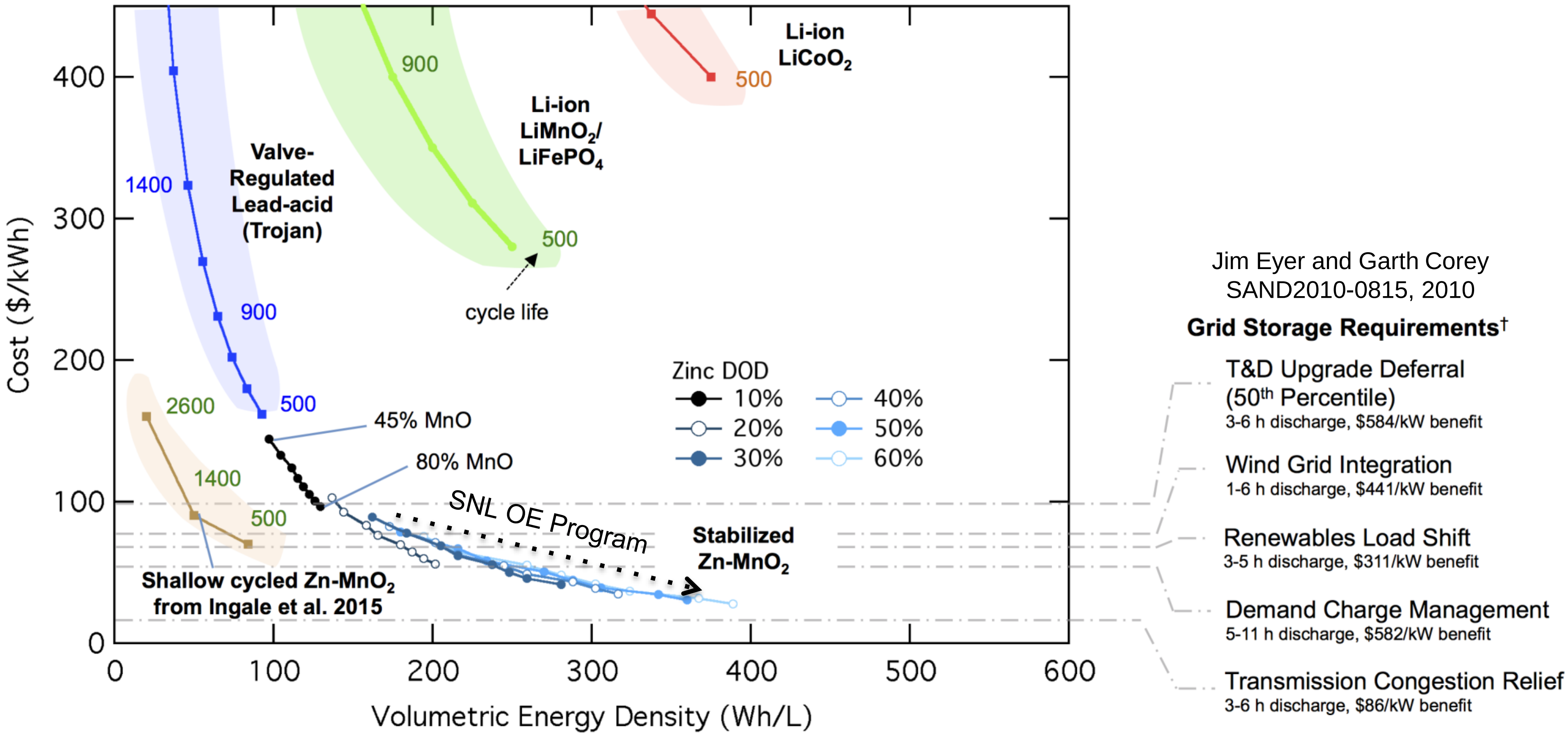
Opportunity exists to Increase Capacity and Decrease Costs



Toward Low Cost/High Volumetric Energy Storage

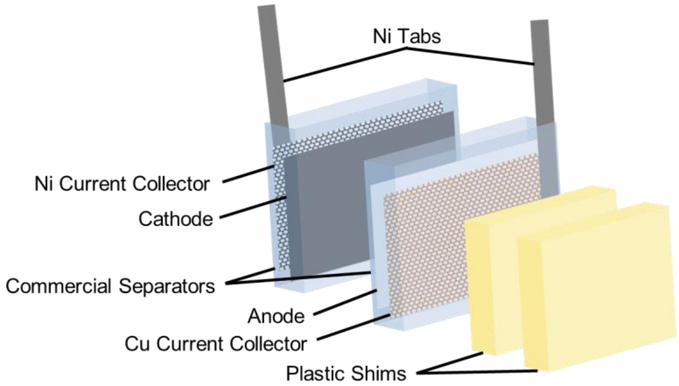
1. Support Limited Depth-of-Discharge Efforts
2. Develop Higher Capacity Batteries

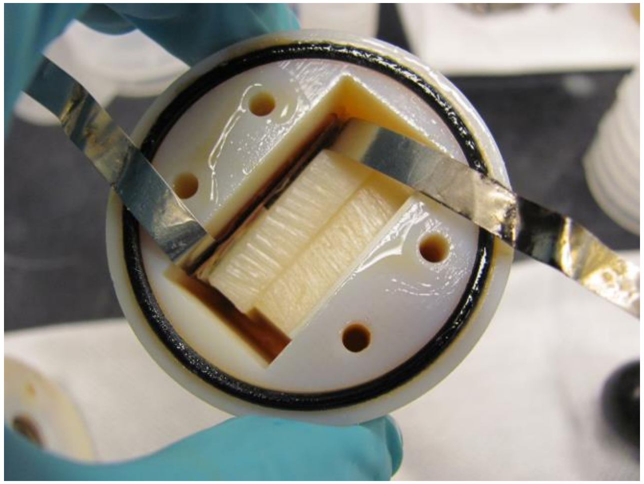
N. D. Ingale, J. W. Gallaway, M. Nyce, A. Couzis and S. Banerjee, J. Power Sources, 276, 7 (2015).

The end

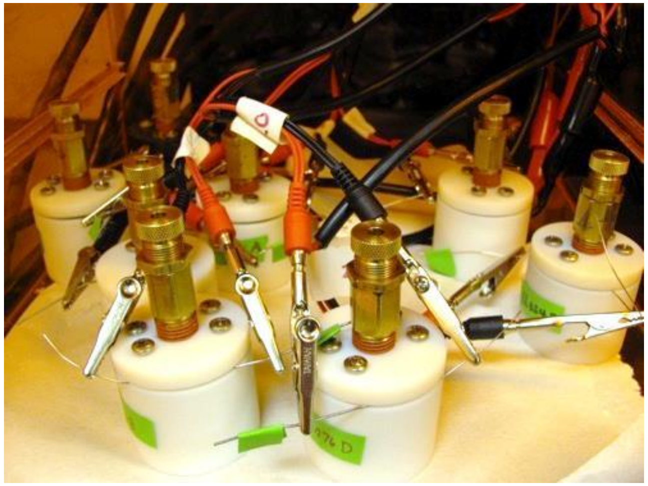
Thank you

Battery Fabrication



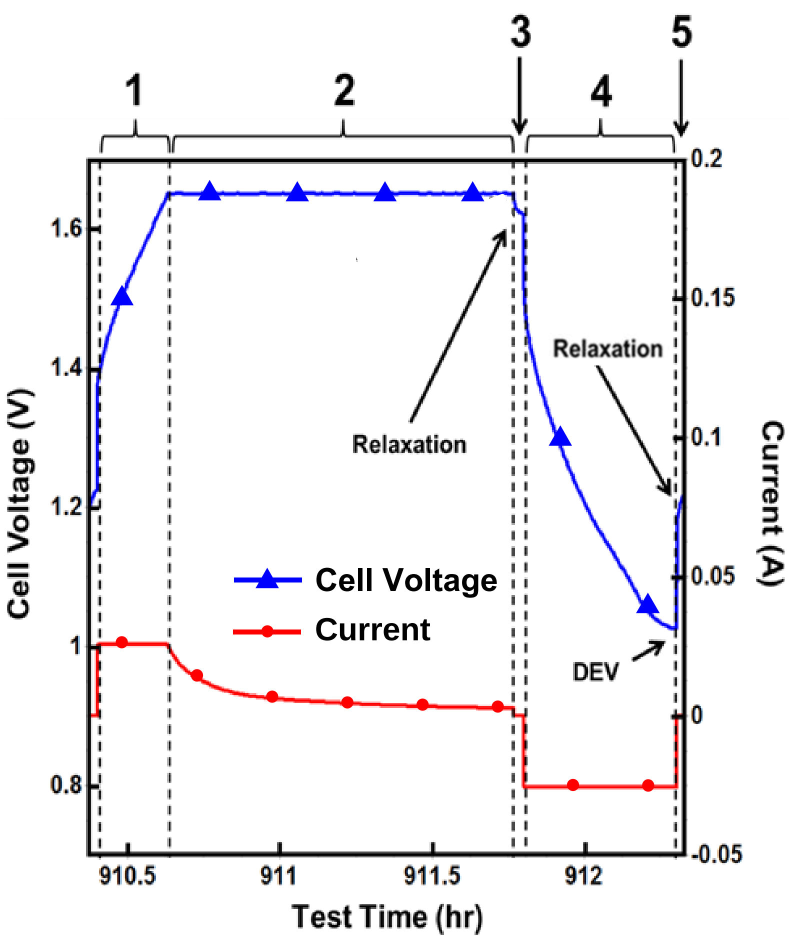


- COTS materials
- 10 vol% TEA added to electrolyte
- 3D printed cells with pressure relief valve
- Cathode-limited cells (< 1.5% DOD on Zn)
- ~ 200 mAh capacity



N. D. Ingale, J. W. Gallaway, M. Nyce, A. Couzis and S. Banerjee, J. Power Sources, 276, 7 (2015).

Cycling Protocol



DOD controlled by *time* and *C-rate*

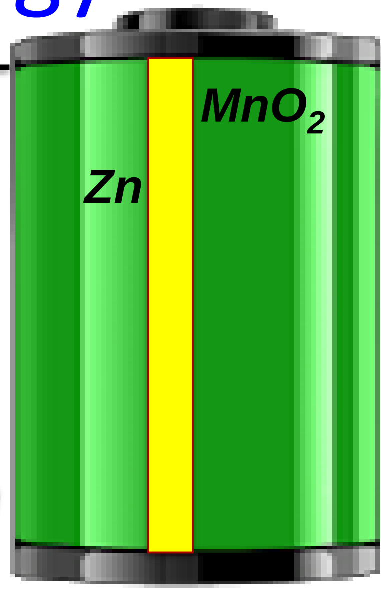
1. Constant current charge
2. Constant voltage charge
3. Rest step
4. Constant current discharge
5. Rest step

$$M \times T \times C = Discharge\ Current$$

M: Mass of Active Material (g)
T: Theoretical Capacity of Material (mAh/g)
C: C-rate (h^{-1})

Low DOD discharge is viable technology

2 e-
= 820 mAh/g



2 e^- = 616 mAh/g

1 e^- = 308 mAh/g

Low % Utilization

Low % Utilization

- Limited DOD provides for highly reversible system
- 2013 Urban Electric Power startup in NYC
- $100 – 150 /kWh

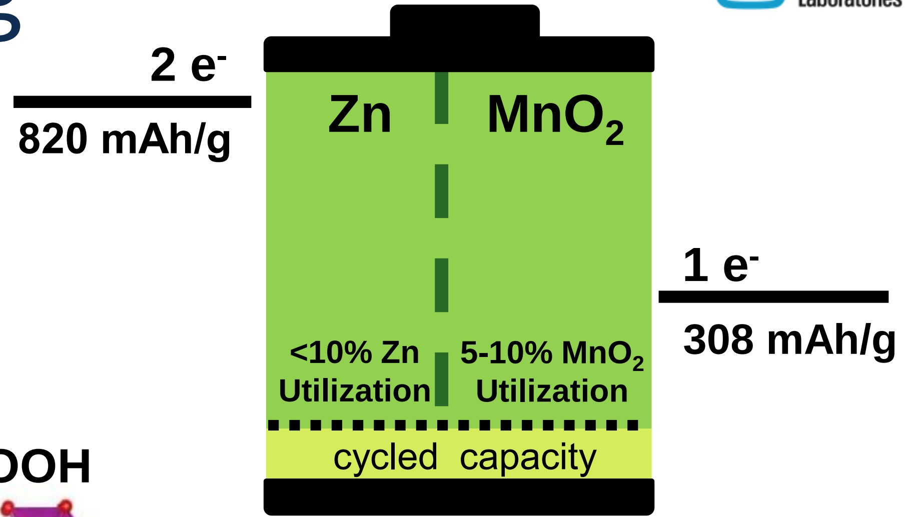
http://www.urbanelectricpower.com

Low Cost
and reversibility
=
Viable Technology

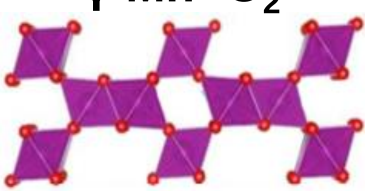
Opportunity exists to drastically increase capacity

Limited DOD Cycling

Reversibility can be maintained when only *a fraction of the first e^- step is cycled.*



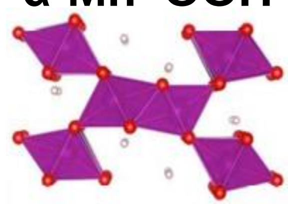
γ-$Mn^{IV}O_2$



Ramsdellite-like (2x1 channels)
Pyrolusite intergrowths (1x1 channels)

Intercalation Regime
$n = {}^{1}/_{x}\ e^-$

α-$Mn^{III}OOH$



Volume expansion
Mn^{3+} (0.645 Å) > Mn^{4+} (0.530 Å)

Mn_3O_4
$ZnMn_2O_4$
Mn_2O_3
$Mn(OH)_2$

Formation of undesirable phases from soluble Mn^{3+}

Cathode issues

- Only 5-10% of total capacity
- Crystal Structure Breakdown
- Inactive Phase(s) formed
- Zinc poisoning

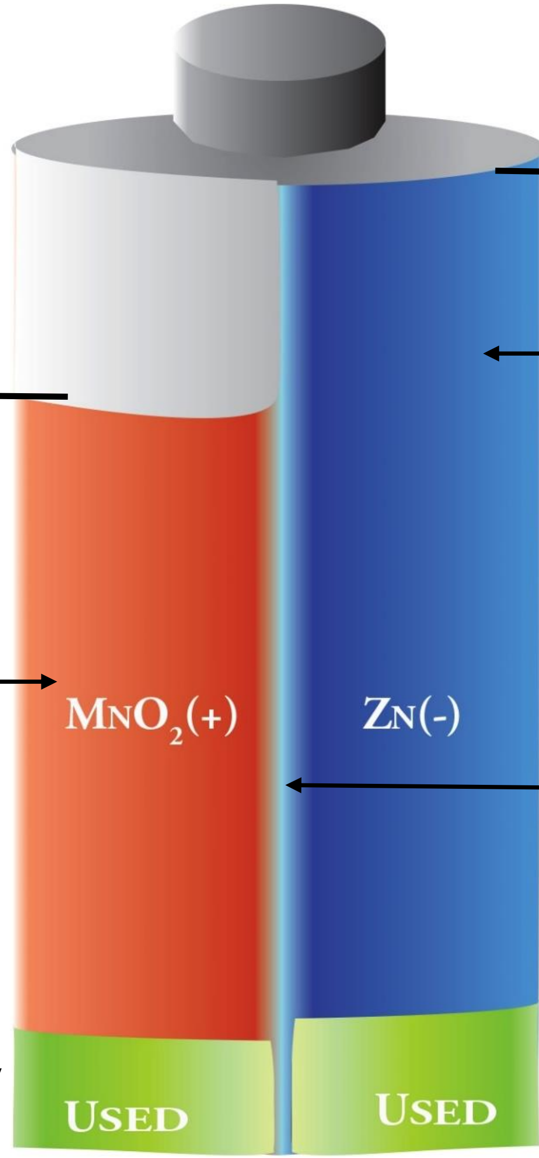
Anode issues

- < 10% of total capacity
- Shape Changes
- Passivation
- Dendrite Formation

- Limited DOD provides for highly reversible system
- 2013 Urban Electric Power startup in NYC
- ~ $100/kWh

- Wh

ALKALINE BATTERY TECHNOLOGY



820mAh/g

- Shape change
- Passivation
- Dendrite formation

617mAh/g

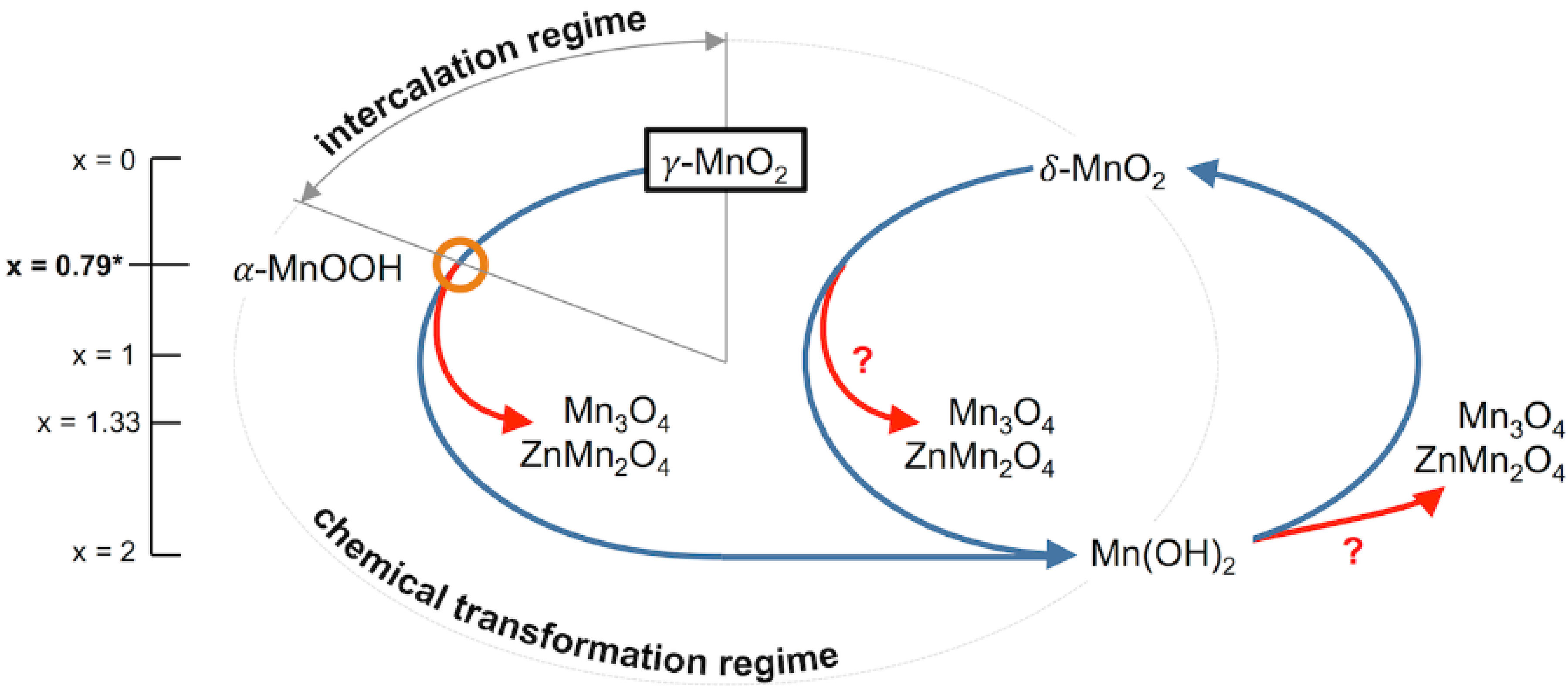
- Crystal structure breakdown
- Formation of Inactive phases
- Zinc poisoning

- Diffusion of zincate ions

5-10% of total capacity

2-8% of total capacity

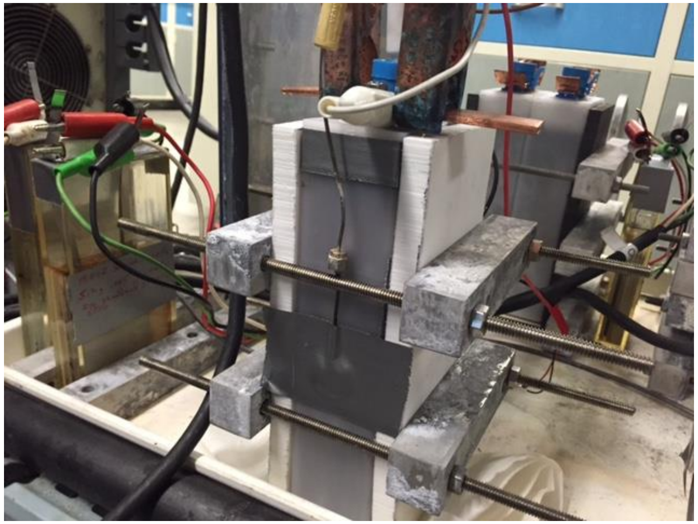
Failure Mechanisms of Cathode

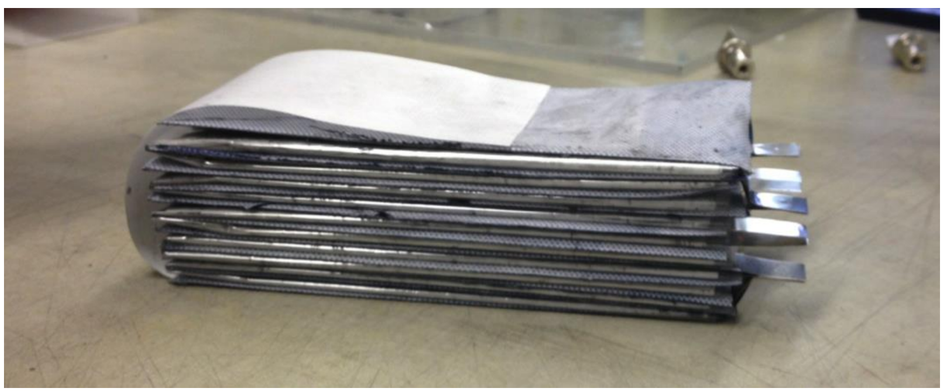


1. Instability of Mn(III) resulting in formation of irreversible $\mathbf{Mn_3O_4}$

2. Zn poisoning forming irreversible $\mathbf{ZnMn_2O_4}$ (even before 1st full 1 e-)

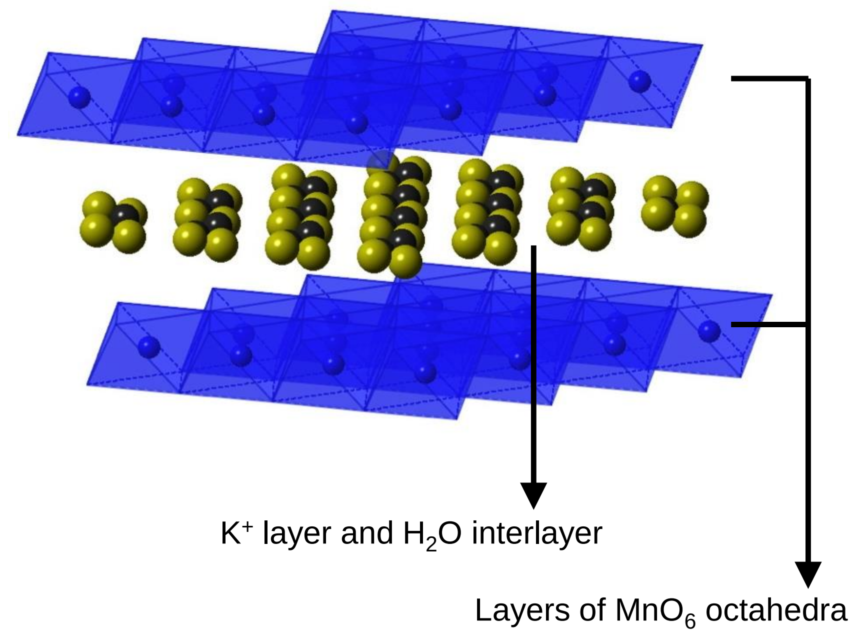
Stabilized Zn-MnO Battery Development (ARPA-E)





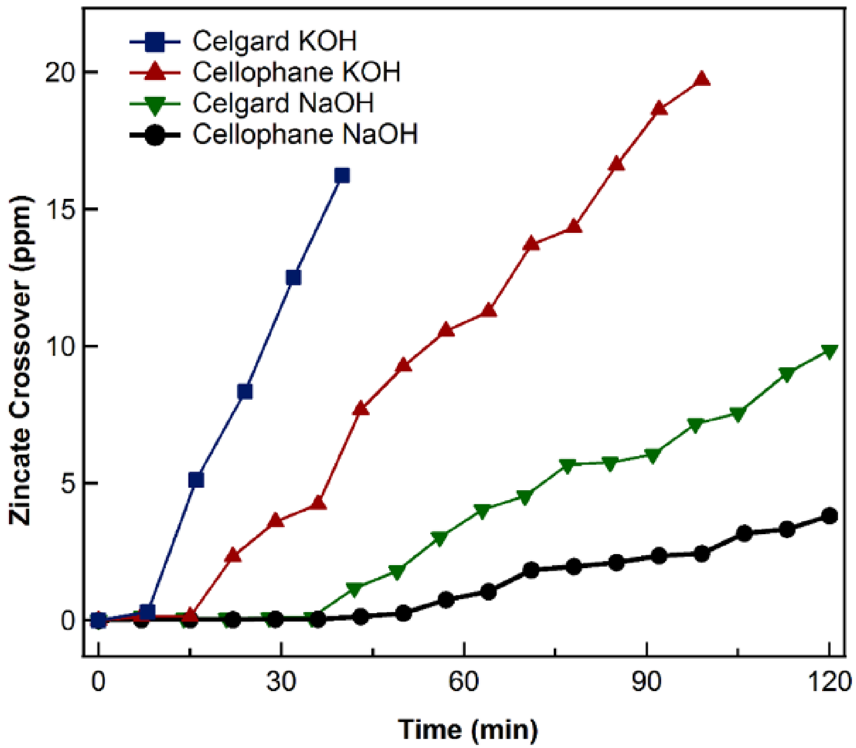
Prismatic battery design for pasted Zn and stabilized MnO

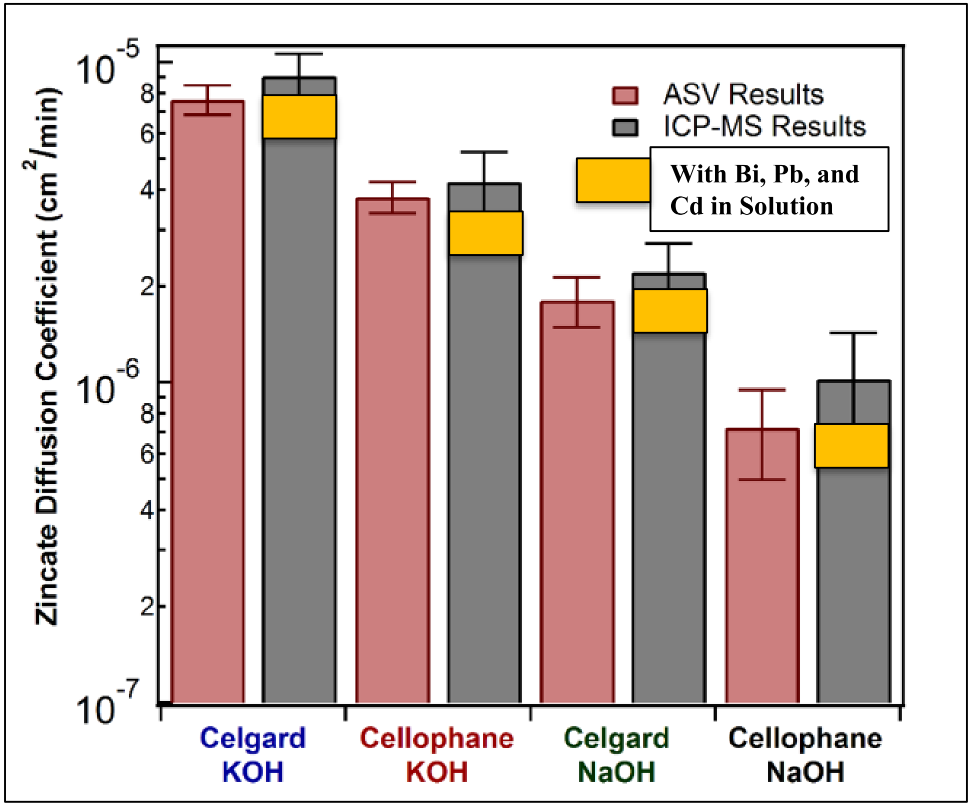
Chemistry relies on formation of a **layered** birnessite MnO_2 structure and **stabilizing** this structure for thousands of cycles.



Two additives stabilize this structure: Bi + “A”

Separators



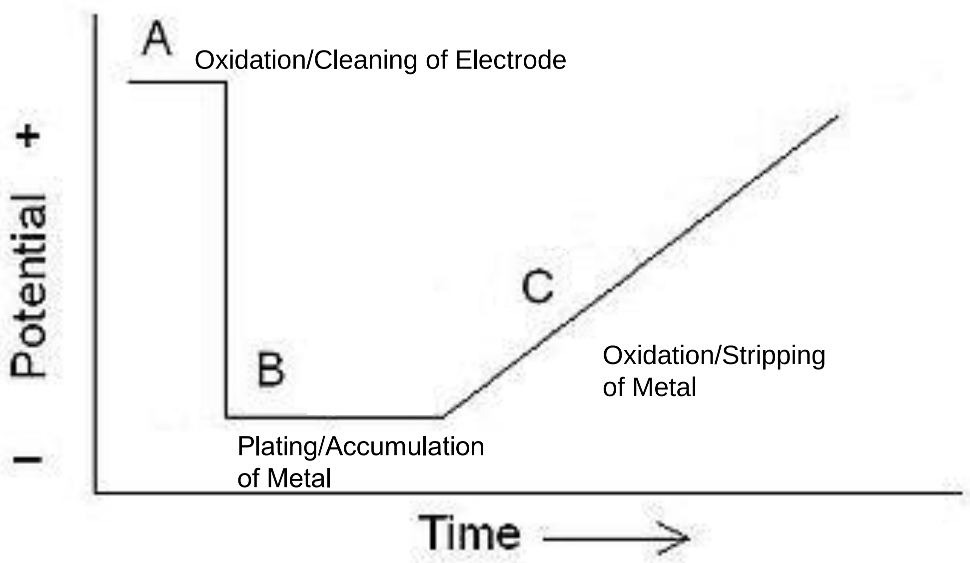


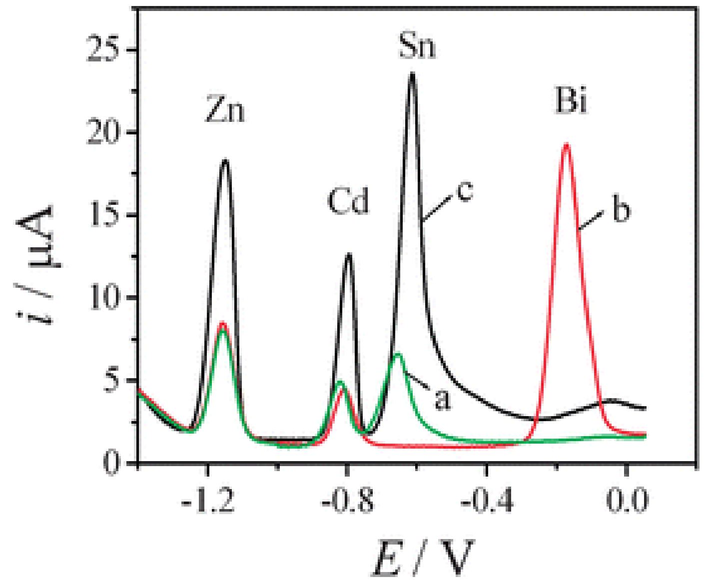
- Compares favorably *vs.* ICP and Complexometric methods
- Faster experiment times, very reproducible, low limit of detection
- First demonstration of ASV measurement of Zinc in alkaline
- Will allow for rapid screening of newly developed membranes

J. Duay *et al. Electroanalysis* **2017**, *http://dx.doi.org/10.1002/elan.201700337.*

Anodic Stripping Voltammetry (ASV)

-Historically done on Hg drop electrodes
-Usually done in buffered solutions





Analyst, 2012,**137**, 614-617

Sensitive
-limits of detection (LOD): ppb levels
Selective
-different metals are resolved by their stripping/oxidation potential

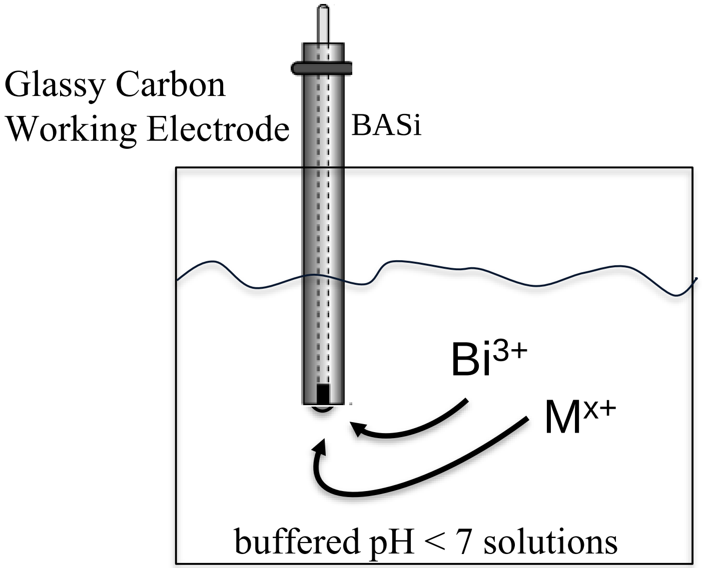
ASV with *in situ* Plated Bi Films

-Bi film electrodes increasingly replacing Hg

Bi film electrodes

-less toxic than Hg
-low sensitivity to dissolved oxygen
-better reproducibility
-no need for electrode conditioning

in situ Plated Bi Films



-Bi is plated onto an passive electrode with the element of interest During stripping, the element of interest is stripped from the Bi film

Typically done in buffered pH ~4 solutions due to insoluble metal oxides at higher pH levels

Alkaline Aqueous Chemistry (pH>14)

Insoluble metal oxides become soluble by hydroxide complexation

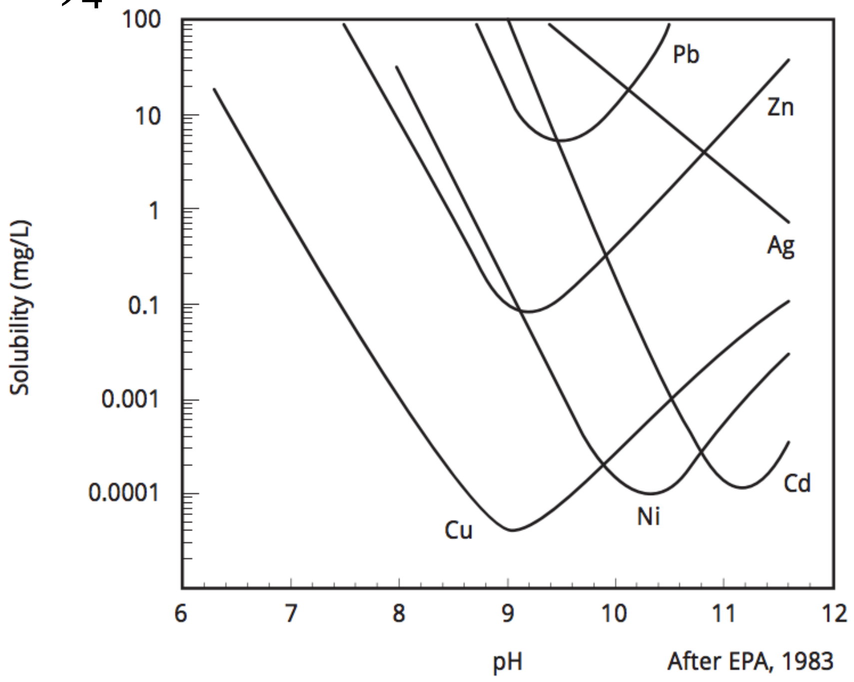
$ZnO(s) + H_2O + 2OH^- \rightarrow Zn(OH)_4^{2-}$

$PbO(s) + H_2O + OH^- \rightarrow Pb(OH)_3^-$

$CdO(s) + H_2O + OH^- \rightarrow Cd(OH)_3^-$

$Bi_2O_3(s) + 3H_2O + 2OH^- \rightarrow 2Bi(OH)_4^-$

This allows for the opportunity to use ASV to measure metal ion species in highly alkaline environments for the first time



Zinc ASV Curves for Various Films

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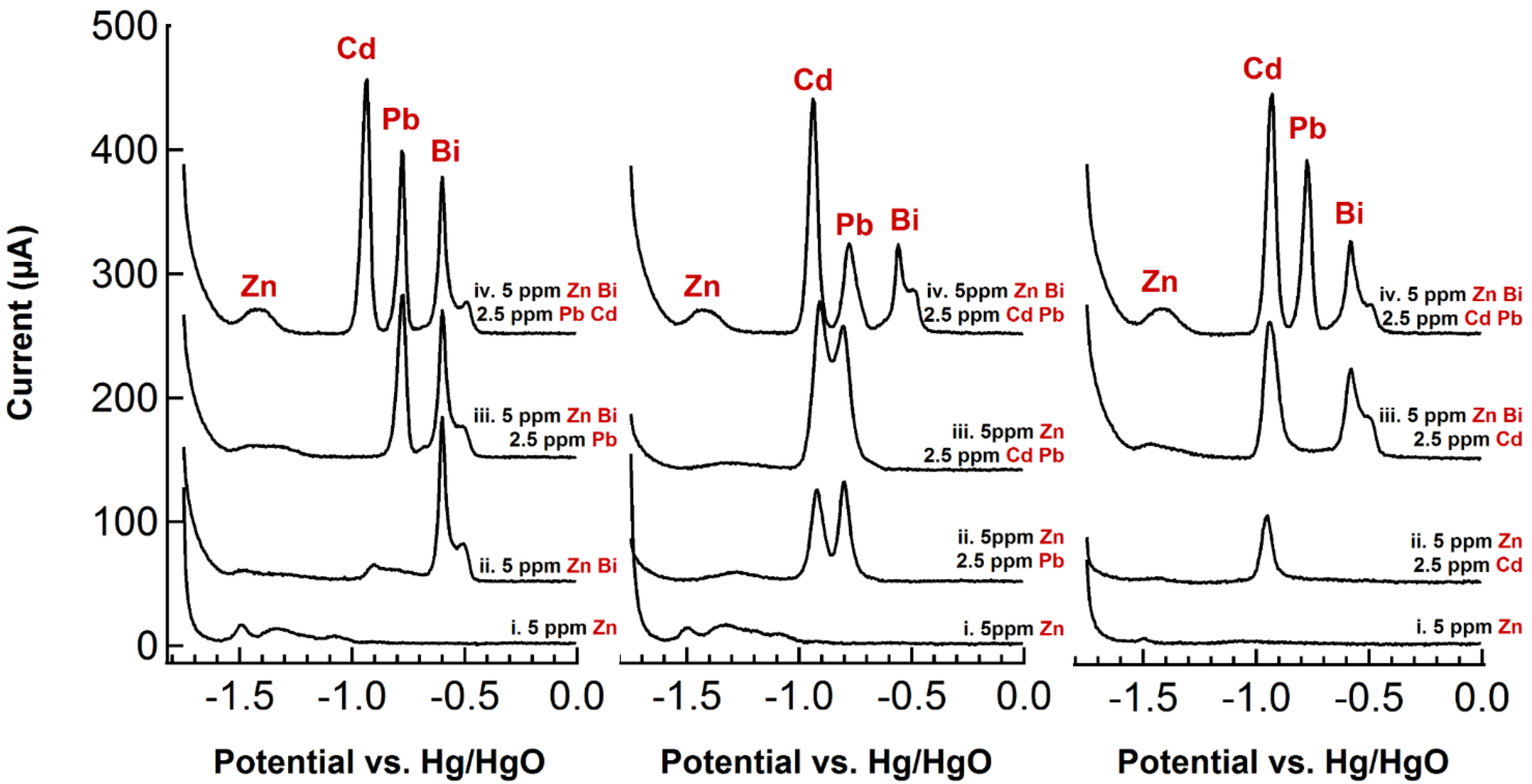
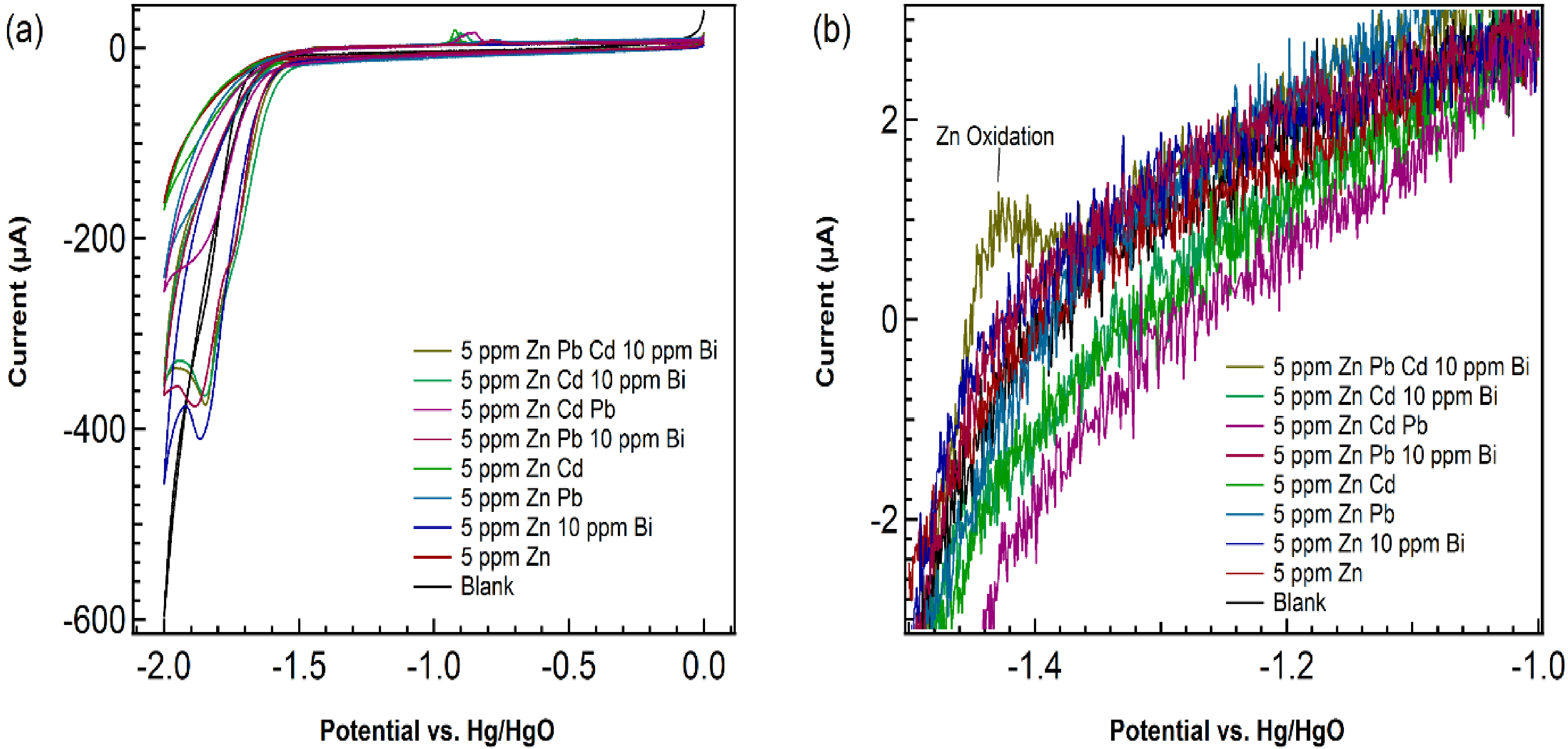


Zinc stripping peak is only well-defined and Gaussian in the presence of Bi, Cd, and Pb….why?

Zinc ASV Curves for Various Films



Zinc stripping peak is only well-defined and Gaussian in the presence of Bi, Cd, and Pb….why?

Need for all three Cd, Pb, and Bi?

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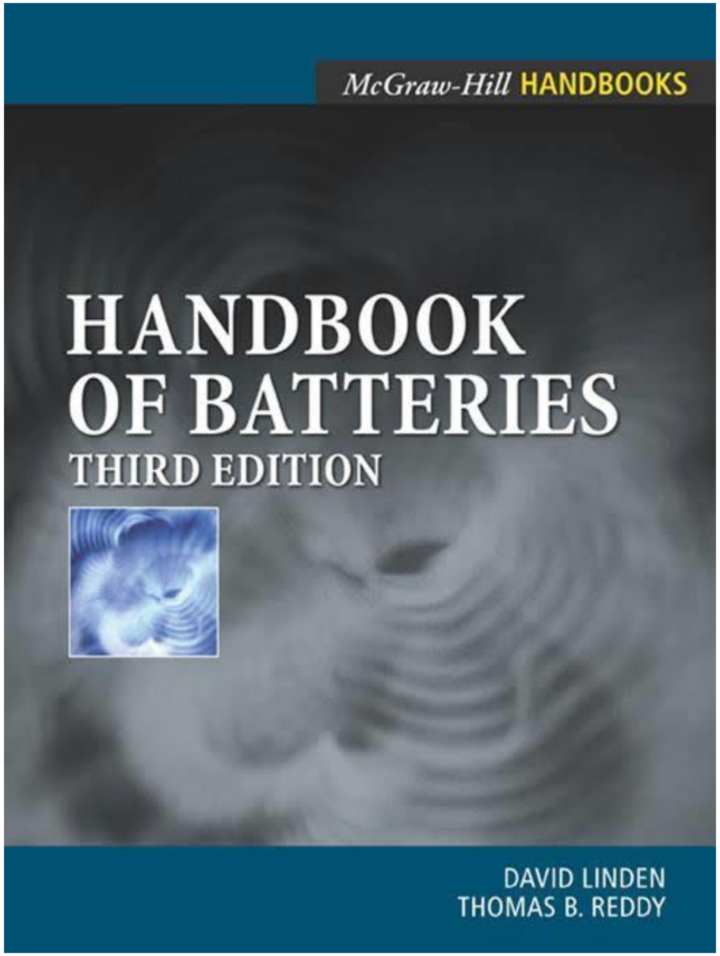
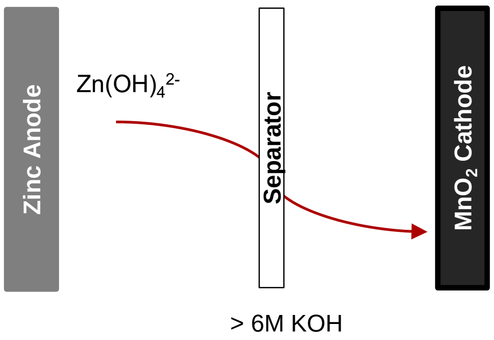
All three have been used as **additives in battery grade Zn** where 'plating' and 'stripping' of Zn is necessary

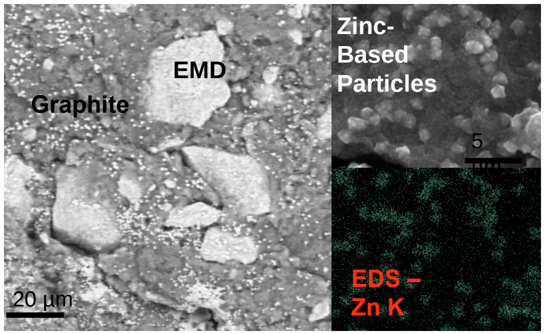
Cadmium (Cd)
-increases hydrogen overpotential
-known to alloy with Zn
Lead (Pb)
-increases hydrogen overpotential
-known as alternative ASV film to Bi
Bismuth (Bi)
-increases hydrogen overpotential



Need for Selective Separators



MnO_2 Cathode After Cycling



Zinc-Based Particles
-Insulating
-Combine with cathode material to form irreversible compounds

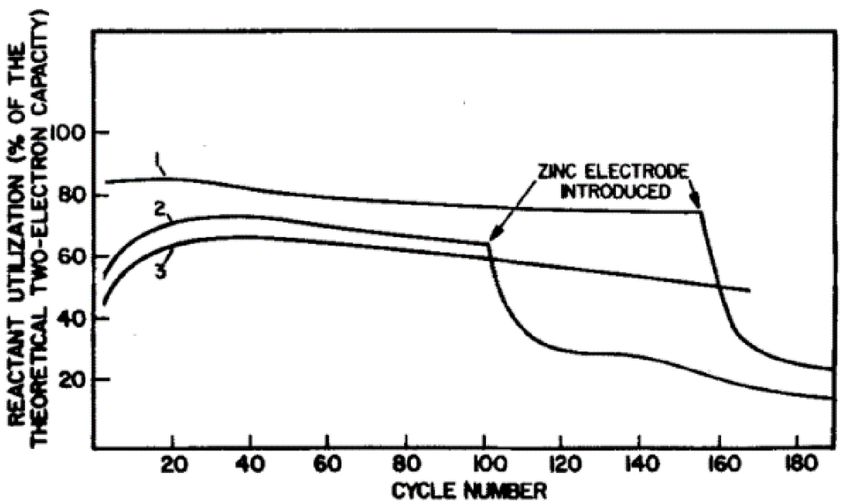
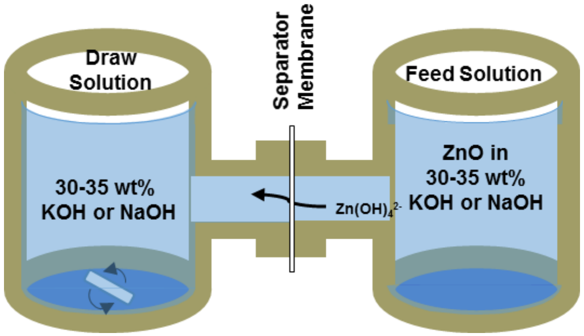


Fig. 5. Effect of the introduction of zinc on capacity retention of modified MnO_2 electrodes: 1) chemically modified electrode; 2) physically modified electrode; 3) physically modified electrode in 9M KOH + 0.1M $Zn(OH)_4^{=}$.

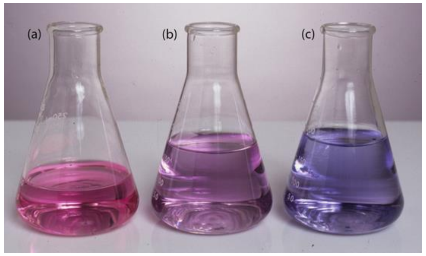
- Research by Ford in the 1980s showed that the MnO_2 cathode could be stabilized at low loadings ***in the absence of Zinc***
- New stabilized 2e- cathodes are 100% reversible ***in the absence of Zinc***

Imperative need for zincate blocking separators

Separators –Analysis Method ?



Sampling, Dilutions, and Calibration Solutions



ICP Metal ion analysis

Perkin-Elmer

Inductively Coupled Plasma – Mass Spectrometer

-time intensive
-lots of glassware
-requires acidic solutions (2% HNO_3)
-requires total dissolved solids <0.2%
-huge dilution >300X
-expensive bulky equipment

Complexometric Titrations

or

UV/Vis Spectrometer

-Difficult Endpoint Determination
-Requires pH $\leq$ 11
-Use of ammonium buffer
-Dilution >20X
-ppm limits of detection

CUNY Battery Research Timeline

anodes

cathodes

Flow-Assisted Zn Anode

Pasted Zn Anode

NiOOH Cathode

Shallow-Cycled MnO_2 Cathode

Stabilized MnO_2 Cathode (Birnessite, Full-Cycle)

Flow-Assisted Ni-Zn Battery: UEP Power Battery, 30 kWh String, 100 kWh Installation (NYSERDA, DOE NETL)

Ni-Zn Vehicle Battery: (NYSERDA)

Shallow-Cycled Zn-MnO_2 Battery: UEP Production Product. <$100/kWh cost, >4000 cycles, Cathode based on 60 mAh/g-MnO_2 (ARPA-E)

Stabilized Zn-MnO Battery: Bismuth-stabilized birnessite concept realized with novel chemistry discovery. *(ARPA-E)*

Focuses on Energy density (Wh/L). Targets <$50/kWh cost, >500 cycles, 180 Wh/L. Cathode based on 600 mAh/g-MnO_2 (NYSERDA)

DEVELOPMENT OF $Zn\text{-}MnO_2$ BATTERY

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Primary
Low Power

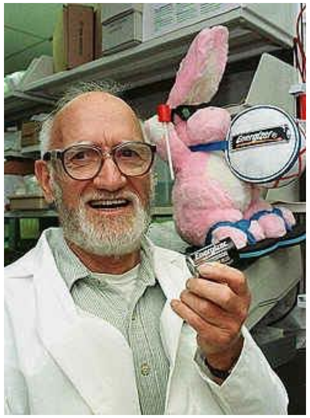
1866

1[st]
MnO_2-Zn
battery

Primary

1950

Alkaline
MnO_2-Zn
battery



Limited Capacity
Poor Energy Density

1970

5% Rechargeable
Capacity

Potentiodynamic
Poor Cycle Life

1980

60-80% Rechargeable
Capacity

Halina Wroblowa

2010-2016

<u>2010-2014</u>:
ARPA-E Support of CUNY shallow-cycle MnO_2

<u>2014-2016:</u>
ARPA-E support of CUNY stabilized full-cycling MnO_2